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| <p>(54) Title: ALKALI METAL FERRATES AND A METHOD OF MAKING THE SAME</p> <p>(57) Abstract</p> <p>Alkali metal ferrates and a method for making the same. The method includes suspending an oxidizable iron-containing particle reactant in a molten phase comprising an alkali metal nitrate reactant and an oxy-alkali metal reactant, and reacting the reactants at a reaction temperature of from about 700 °C to about 1100 °C.</p> | | |

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ALKALI METAL FERRATES AND A METHOD OF MAKING THE SAME

Field of the Invention

This invention relates to alkali metal ferrates and a method for making the
5 same.

Background of the Invention

Iron exists in combination with other elements in a variety of oxidation
states. While iron having an oxidation state of +2 or +3 is common, compounds
in which iron has an oxidation state of +4 or greater (hereafter iron (IV or
10 greater)) have been known for a number of years. Of particular interest are a
class of alkali metal salts of iron (IV or greater) ferrates. These compounds are
of interest because they are extremely strong oxidizing agents in aqueous
solutions, as well as metal precipitators/coagulants.

A number of potential uses for these ferrate compounds have been
15 identified. These uses take advantage of two important characteristics of
ferrates in solution. As previously mentioned, these ferrates are strong oxidants
and as such have utility in food processing, catalytic chemistry, pulp and paper
processing, disinfection, and biocidal treatment of contaminated waste waters.
Ferrates also act as coagulants and as such have been demonstrated to help in
20 the removal from waste water of mercury, copper, zinc, lead, cadmium,
manganese, nickel, chromium, silver, aluminum, beryllium, cobalt, iron,
molybdenum, thallium, vanadium, and arsenic. Ferrates have also been
demonstrated to act as coagulants for the removal of radionuclide material,
including americium, plutonium, and uranium.

25 Despite these promising uses, ferrate compounds have not found
widespread use due to difficulties in the production of large quantities at
commercially practical prices. Past methods have exhibited yields in the range
of 5% to 40% high oxidation state iron, while the present invention offers yields
in the range of 60% to 80%.

30 U.S. Pat. No. 5,217,584, by Deininger, teaches several methods of
producing ferrate-containing materials. One such method, as taught in
Deininger involves the reaction of a sodium hypohalite or halogen gas in an

aqueous sodium hydroxide solution with iron salts, producing Na_2FeO_4 . The sodium in this compound can be replaced by potassium by the addition of KOH. This and several related processes are commercially inefficient, however, due to the need to remove the ferrate products from the aqueous solution and the relatively unstable nature of ferrate products in water.

Electrolysis techniques have also been used to react alkali metal nitrates with various iron sources. These methods also are not commercially viable due to small yields, anode passivation, and the need to remove the desired end product from the aqueous reaction mixture. Another process involves the use of a beta-ferrate oxide as the iron precursor in either a hypohalite or electrochemical oxidation reaction. This process appears to require the use of iodine- or tellurium-containing salts as stabilizers and also requires the removal of the desired end products from an aqueous solution.

One attempt to address the difficulties found in the aqueous-based ferrate production processes involved the use of high temperature reactions using solid reactants, and reference is made to Thompson, U.S. patents 4,385,045; 4,545,974; and 4,551,326. Thompson's procedures result in end products which unfortunately demonstrate a number of commercial disadvantages, of which the most important may be that the end product is a very hard solid mass of fused ferrate. Not only may this hard solid mass cause damage to a reaction chamber when removal is attempted, but it also may be difficult to convert to a commercially usable form (preferably a granular, easily dissolvable product). In addition, the hard solid mass produced as described above may have been incompletely converted to the Fe^{+4} or greater oxidation state, conversion occurring primarily at the surface of the iron-containing raw materials.

For ferrate products to become commercially feasible for most applications, an inexpensive and easily usable form of alkali metal ferrates is needed. Such products should be high in iron (IV or greater) ferrate, have minimal amounts of residual nitrate reactant, and should exist in an easily produced, granular form.

Summary of the Invention

One embodiment of the present invention provides for a readily friable or granular source of iron (IV or greater) ferrate and a process for the commercially feasible production thereof. One characteristic of this alkali metal ferrate is its
5 granular or readily friable nature as a thin, sheet-like readily crushable reaction product. This physical property facilitates preparation of an easily dissolvable, storable and transportable product.

A preferred embodiment of this invention provides a product containing iron (IV or greater) at greater than 50 percent by weight. Most preferably, at
10 least about 60 atomic percent of iron in the product is iron (IV or greater). Remaining nitrogen-containing components desirably are less than 5 percent by weight of the final product, and preferably less than 2%. The resulting product desirably contains at least about 7% by weight of silicon oxide, and about 2% by weight of Al_2O_3 .

15 Another embodiment of this invention relates to a method for making a friable alkali metal ferrate composition. Briefly, this method involves the step of forming a reaction mixture including an oxidizable iron source, an alkali metal nitrate reactant, and an oxy-alkali metal reactant. The reactants are heated to a reaction temperature from 800°C to 1100°C for a time from five minutes to four
20 hours to create a reaction product. Preferably, heating is carried out in such a way that the final reaction temperature is achieved as quickly as possible.

In one embodiment of this invention the reaction product is rapidly cooled, resulting in a readily friable reaction product. In a further embodiment of this invention, the reaction product is held at an elevated temperature of 600°C to
25 800°C in a reaction atmosphere where the log partial pressure of nitrogen is less than 0.5 and the log partial pressure of oxygen is between -0.5 and 1.5. This is done to reduce the amount of remaining nitrogen-containing components in the reaction product.

In a preferred embodiment of this invention, nitrogen-containing gases,
30 primarily NO_2 and NO , that are released during the reaction are recycled for use in subsequent reactions in the form of alkali metal nitrates by known means. In

another embodiment of this invention a CO₂ backflow is introduced into the reaction apparatus to assist in the reduction of excess hygroscopic KOH.

To carry out the described reaction, the reactant formulation must be heated in a heating apparatus. In one embodiment the heating apparatus is a high temperature fixed batch kiln or oven. In another embodiment of the invention, the heating apparatus is a rotary kiln, and the reactants are added directly to the primary heating zone of the kiln via an internal conveyor. The kiln desirably includes a transport element such as a helical drive or movable shoes capable of facilitating the continuous movement of material in the kiln. However, the preferred embodiment of the invention involves a heating apparatus where the reaction products are moved through one or more heating zones in a furnace by a conveyor system utilizing reaction trays or the like that are conveyed through the heating zones.

A number of variables such as reaction temperature, reaction time, cooling time, molar relationships of the reaction components, choice of iron source, choice of alkali metal component of the reactants, and reaction atmosphere may be varied to create additional embodiments of this invention.

Description of the Drawings

Figure 1 is a reaction time versus temperature graph which is exemplary of one embodiment of the invention.

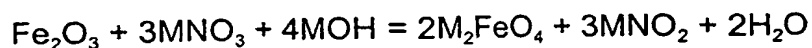
Figure 2 is cutaway side view of one embodiment of a conveyor processing system which uses a tube furnace.

Detailed Description of the Preferred Embodiment

In accordance with the described invention, alkali metal ferrates may be produced in an oxidation reaction in which oxidizable iron, preferably Fe₂O₃, is reacted with an alkali metal nitrate and an oxy-alkali metal reactant under temperature and time conditions producing a high yield of iron (IV or greater) ferrates. Preferably, the reactions proceed in accordance with the following equations:



or



where M represents an alkali metal, desirably potassium or sodium.

A number of iron oxide sources can be used in practicing this invention.

- 5 These include but are not limited to magnetite, hematite ore, wustite ore, geothite ore, lepidocrocite ore, metallic iron, pickling iron, or an iron oxide-rich flue dust derived from iron or steel production. In some cases the iron may have a perovskite structure (See, Nature, Vol. 387, p. 653-654 (1997)).

- A preferred iron source is hematite ore, and particularly hematite ore that
10 contains from about 5% to 10% by weight of SiO_2 . A greatly preferred source is hematite ore and particularly hematite ore that contains silicon dioxide at a concentration of from 5% to 10% by weight and preferably about 7% by weight, and Al_2O_3 at a concentration of approximately 1.0 to 2.5% by weight, the ore being particulate in nature and having an average particle size in the range of
15 about 1.0 to 2.0 microns and preferably about 1.5 microns.

- One preferred iron source is Sedona Red iron oxide (Arizona Oxides, Prod. No. AZO-101), containing about 90% Fe_2O_3 and about 7% SiO_2 . The greatest reaction yields have been observed using this preferred iron source, although other iron sources can be used. One might also process a different
20 iron source so that it has a final chemical composition comparable to that of the preferred iron source, AZO-101.

- A number of alkali metal nitrates and oxi-alkali metal reactants can be used in the invention, such as the nitrates, oxides, peroxides, and hydroxides of lithium, sodium, potassium, rubidium, and cesium. Preferred embodiments of
25 this invention use the alkali metals sodium (Na) or potassium (K). Having chosen an alkali metal, the appropriate alkali metal nitrate reactant is selected. Preferred embodiments of this invention use the alkali metal nitrates potassium nitrate (KNO_3) or sodium nitrate (NaNO_3).

A wide range of suitable oxy-alkali metal reactants may be employed.

- 30 Such reactants include KOH , K_2O , K_2O_2 , K_2O_3 , KO_2 , NaOH , Na_2O , Na_2O_2 , Na_2O_3 ,

NaO₂. The preferred oxy-alkali metal reactant is one or more of KOH, K₂O, NaOH, and Na₂O.

Notwithstanding the above, alkaline-earth metals may be used in place of the alkali metals previously discussed. These include beryllium, magnesium, calcium, strontium, and barium. The result would be an alkaline-earth metal iron (IV or greater) ferrate such as MgFeO₄ or MgFeO₃.

Another parameter which can be important in the selection of reactants is the presence of silicon oxides. In a preferred embodiment, at least 6% by weight of the iron oxide reactant is silicon oxide. Most commonly, this component will be naturally present in the iron source. This component is believed to further enhance the creation of a readily friable reaction product.

Preparation of a reactant formulation involves intimately mixing of the reactants to ensure high reaction efficiency. While there are many methods of mixing such reactants known to the art, a preferred embodiment of this invention involves the creation of small granular pellets, each containing an intimate mixture of the chosen reactants. In a preferred embodiment these pellets have an average diameter in the range of 0.2 to 1.5 mm, preferably about one mm. Each pellet comprises a plurality of finely divided iron oxide particles distributed through its bulk and in close proximity to the other reactants, the iron oxide particles being desirably in the range of 1.0 to about 2.0 microns in diameter, and preferably 1.5 microns in diameter.

While many techniques are known in the art to form such reaction pellets, one acceptable method is to thoroughly mix the reactants with a ring & puck mixing apparatus. An optional binding agent may also be added to the mixture to enhance pellet formation. Finally, the resulting pellets are oven dried to a pre-selected green strength and desirably are separated by a pellet sizer. One readily available device for the creation of such pellets is a Carver press.

As illustrated in Figure 1, the resulting formulation is supported in a reaction vessel and is heated to a temperature between about 800°C and about 1100°C. In a preferred embodiment the reaction temperature is from about

900°C to about 1000°C, reaction temperature of approximately 950°C being particularly preferred.

The reactants are held at the desired reaction temperature (or in a selected temperature range) for a time period from approximately 1 minute to approximately 4 hours. In one embodiment, the reactants are held for a time period from approximately 5 minutes to approximately 90 minutes. Preferably, the reactants are held at the reaction temperature for a time period from approximately 10 minutes to approximately 30 minutes, with approximately 10 minutes being particularly preferred.

During the reaction period, the alkali metal nitrate and oxy-alkali metal reactants will melt at temperatures below the reaction temperature, e.g., at about 200°C to 300°C. Certain reactants (e.g., KOH, KNO₃) may form a eutectic molten phase. In any event, the molten phase surrounds and suspends the iron-containing particles and creates suitable reaction conditions for the formation of iron (IV or greater) ferrates. It will be understood that a very homogeneous mixture of the reactants will promote this process.

Without the intention of being limited by the following teaching, it is believed that the size and distribution of the iron particles may be important to the reaction efficiency of the present invention. This may be the result of a "Chinese egg" phenomenon where the reactive nitrates will initially react with iron molecules located closest to the periphery of the iron particle. Over time the reactive nitrates will diffuse further into the particle and react with iron molecules in the interior of the particle.

Ferrate yields are increased by rapidly heating the reactants to the final reaction temperature, rather than slowly heating them. In a rotary kiln, rapid heating may be achieved by adding the reactants into the primary (that is, hottest) heating zone via a feed tube. This feed tube delivers the reactant formulation past the cooler peripheral heating portions of the heating apparatus into the hotter primary heating zone, often near the center of the kiln. The reactant formulation may be preheated, e.g., to a temperature from about 400°C

to about 650°C, prior to being placed in the heating apparatus so that it can be brought in a more rapid and controllable manner to the reaction temperature.

In a preferred embodiment of this invention, the reactant formulation is rapidly heated to its reaction temperature within an elongated furnace enclosure, e.g., a tube furnace. Optimally, the reactant formulation can be transported through the tube furnace by a conveyor such as a train of crucibles, an endless conveyor belt, etc., the heating zones of the furnace being arranged to facilitate the rapid heating of the reactants to the reaction temperature.

Handling of the reaction products after the desired reaction time may also be important. It is believed that quickly cooling the reaction product below the primary reaction temperature soon after the completion of the desired reaction time serves to "quench" undesirable back reactions that may reduce overall yield. The temperature must be reduced below 800°C to achieve this quenching. It has also been found that a final rapid cooling of the reaction products to a temperature below 100°C increases the friable nature of the final alkali metal ferrate product, presumably by forming fine cracks as the product contracts. It is believed that a reaction product cooling rate of greater than 20°C per minute enhances this effect. This cooling step may occur directly after the primary heating time, or it may follow the secondary holding period described in the following paragraph.

It is preferable to reduce the amount of residual nitrogen-containing chemicals in the reaction product. It has been found that, following the primary heating step discussed above, cooling the reaction products to a temperature from 600°C to 800°C in a proper reaction atmosphere can reduce the amount of residual nitrogen-containing compounds in the reaction product by allowing additional release of volatilized nitrogen-containing compounds. Preferably, this reduced temperature will be maintained for a period from 5 minutes to 1 hour, preferably 15 minutes. Also, it is preferred that the reaction atmosphere in this step have a log partial pressure of nitrogen less than 0.5 and have a log partial pressure of oxygen between -0.5 and 1.5 to reduce the remaining alloy metal

nitrate concentration in the reaction product to less than 5 percent, preferably less than 2 percent.

In practicing this invention, it is desirable to be able to capture and reuse NO_x gas released during the reaction steps. A number of readily available means can be used to achieve this capture. One example of such commercially available means is the Ejector-Venturi gas scrubber sold by Schutte & Koerting.

Again, the means for recycling the NO_x gases released from the reactants to alkali metal nitrate are readily available. In one such means, the captured nitrogen-containing exhaust gases passed through an alkali hydroxide-containing solution to convert the NO_x gases to alkali metal nitrate. Preferably the alkali hydroxide is potassium hydroxide. This reaction likely results in the formation of both potassium nitrate and potassium nitrite. The desired nitrate form can be selectively purified by a number of standard chemical techniques. One example would be to purify the potassium nitrate via fractional crystallization.

To reduce the amount of hygroscopic potassium hydroxide one may provide a back flow of CO_2 into the heating apparatus from its exit end. Preferably, this back flow would have a flow rate sufficient to maintain at least a 1 to 2 mole ratio of CO_2 to excess KOH. It is believed that the presence of the CO_2 will remove the hygroscopic residual potassium hydroxide by converting it into potassium carbonate.

Another important parameter in this invention is the molar relationships between the various reactants. It has been found (and demonstrated in the following examples) that while creation of iron (IV or greater) ferrates occurs with a mole ratio of alkali metal nitrate to Fe_2O_3 of 2.5, improved yields are found when the mole ratio of alkali metal nitrate to Fe_2O_3 is greater than 3.0.

It has also been found that addition of an oxy-alkali metal reactant increases the yield of iron (IV or greater) ferrates. In a preferred embodiment, it has been shown that the addition of a minimum of 0.2 moles of KOH per mole of Fe_2O_3 dramatically increases the yield of iron (IV or greater) ferrates. This

increase in yield is further enhanced as the concentration of potassium hydroxide is increased to 0.5 moles of KOH per mole of Fe_2O_3 .

In achieving commercially viable production scales of this alkali metal ferrite reaction product, any of several heating apparatuses can be used. A large scale batch method is possible using standard oven or kiln processes. Desirably, however, a continuous process is used in which reactants are charged to an elongated furnace and are conveyed through the furnace at a rate that enables the ferrate-forming reaction to occur, to provide high yields of Fe (IV or greater). A rotary kiln may be used in which the reactant formulation is charged to the downward sloping rotating kiln. The rotation of this kiln, which may have spiral internal groove designed to urge the reactant formulation along the axis of the kiln as the kiln rotates through one or more heating zones. Such rotary kilns are known in the art.

The preferred technique utilizes a continuous belt-type conveyor system as shown in Figure 2 to move the reactant formulation through one or more heating zones of a furnace. A source of reactants 1 supplies the necessary reactants to a continuous heat resistant conveyor belt 3 via a delivery tube 2. The endless belt 3 travels about rollers 4 and 5 at opposite ends of the furnace, and conveys the reactants through a tube furnace 7 having one or more heating zones 9 & 10, ultimately delivering the reaction products to a receiving bin 6. The dwell time of the formulation in a heating zone is controlled to yield the desired time in the reaction temperature range. This could be achieved by either halting the advance of the conveyor system for the desired reaction time, or, preferably, by timing the advance rate of the conveyor system so that the reactants' movement through the heating zone coincides with the desired reaction time.

In a preferred embodiment the reactant formulation is advanced from the primary heating zone 9 to a second heating zone 10 where the reactants are subjected to a second, lower, temperature for a desired period of time as previously discussed. In another embodiment the tube furnace has means for

removal of gaseous reaction products 8. The captured nitrogen-containing gaseous reaction products may be recycled as previously discussed.

As already mentioned, it is desirable to include in any heating apparatus a means for capturing NO_x gas released from the chemical reaction. Preferably, exhaust gases are scrubbed to recover nitrogen oxides, which are recycled back to an alkali metal nitrate form and used in subsequent reactant formulations. An alkali hydroxide-containing solution can be used to convert the NO_x gases released from the reactants to alkali metal nitrate. Preferably the alkali hydroxide is potassium hydroxide. As discussed above, this reaction likely results in the formation of both potassium nitrate and potassium nitrite. The desired nitrate form can be selectively purified by a number of standard chemical techniques. One example would be to purify the potassium nitrate via fractional crystallization.

Without intending to be limited by the following, it is believed that the alkali metal ferrate product described herein possess an additional unique and commercially important characteristic. In one of its important uses alkali metal ferrates are added to waste water for purification. This purification is achieved via both oxidation and coagulation. In the coagulation process it is desirable to reduce the volume of water retained within the precipitate. When using the alkali metal iron (IV or greater) ferrates of this invention a noticeably more compact precipitate has been observed. This results in less waste material for final disposal. It is believed that this unique feature is due to a conversion of the iron ferrates of this invention to goethite (FeOOH) when dissolved in an aqueous solution. Goethite is believed to retain less water during coagulation than other forms of reduced ferrate manufactured by different processes, thereby resulting in a smaller weight and volume of waste material.

The present invention is further described in connection with the following examples, which illustrate the invention in a non-limiting fashion.

EXAMPLES

30 Sedona Red iron oxide having the following physical and chemical characteristics was used in each example:

| | |
|--|-----------------------------|
| Bulk Density (lb./cu.ft.) | 55 |
| Specific Gravity (@ 20°C) | 4.9 |
| Melting Point | Decomposes @ 1538°C |
| Mesh Size | 0.01% Retention on 325 Mesh |
| Hegmen Grind | 7± |
| Oil Absorption | 22 |
| Average Particle Size | 1.5μ |
| Moisture Content | 0.1% |
| L.O.I | 0.07% |
| Solubility in Water | 0.22% |
| pH | 8.0 |
| Iron Oxide, Fe ₂ O ₃ | 89.5%-91.0% |
| Silicon Dioxide, SiO ₂ | 7.0% |
| Calcium Oxide, CaO | 0.13% |
| Aluminum Oxide, Al ₂ O ₃ | 1.9% |
| Titanium Dioxide, TiO ₂ | 0.38% |
| Potassium Oxide, K ₂ O | 0.28% |

Example 1

A series of reactant formulations were prepared for the purpose of evaluating the effect of temperature upon iron (IV or greater) ferrate conversion.

- 5 Sedona Red iron oxide, potassium nitrate, and potassium hydroxide were mixed thoroughly by use of a ring mill. Aliquots of the formulation were heated in a muffle furnace to temperatures from 900°C to 1000°C for either 0.5 or 1.0 hours. The resulting reaction product was analyzed for iron (IV or greater) ferrate content by standard methods. The reactant formulations and percent of the iron
- 10 converted to Fe⁺⁶ are found on the table below.

| °C | Moles KNO ₃ per Mole Fe ₂ O ₃ | Moles KOH per Mole Fe ₂ O ₃ | HOURS | % Converted to K ₂ FeO ₄ |
|------|--|---|-------|--|
| 900 | 4.5 | 0.3 | 1.0 | 4 |
| 950 | 4.5 | 0.3 | 0.5 | 51 |
| 950 | 4.5 | 0.3 | 0.5 | 58 |
| 950 | 4.5 | 0.3 | 0.5 | 51 |
| 950 | 4.5 | 0.3 | 0.5 | 60(?) |
| 925 | 3.5 | 0.3 | 0.5 | 24 |
| 1000 | 3.5 | 0.3 | 0.5 | 49(?) |
| 975 | 3.5 | 0.5 | 1.0 | 57 |

Example 2

- To determine optimum heating times, various reactant formulations were prepared. Each of these preparations incorporated Sedona Red iron oxide, potassium nitrate concentrations ranging from 3.2 to 4.0 moles KNO₃ to Fe₂O₃, and potassium hydroxide concentrations ranging from 0.2 to 0.5 moles KOH to Fe₂O₃. The resulting formulations were intimately mixed via a ring mill and were heated in a muffle furnace at 950°C for a period of 0.5 to 2.0 hours. The reactant formulations and percent of the iron converted to Fe⁺⁶ are found in the table below.

| °C | Moles KNO ₃ per Mole Fe ₂ O ₃ | Moles KOH per Mole Fe ₂ O ₃ | HOURS | % Converted to K ₂ FeO ₄ |
|-----|--|---|-------|--|
| 950 | 3.2(?) | 0.3 | 0.5 | 63(?) |
| 950 | 3.3 | 0.3 | 1.0 | 53 |
| 950 | 3.5 | 0.5 | 0.5 | 71 |

| | | | | |
|-----|--------|-----|-----|---------|
| 950 | 3.6(?) | 0.2 | 0.5 | 55.8(?) |
| 950 | 3.6 | 0.4 | 0.5 | 49.5 |
| 950 | 3.7 | 0.3 | 1.0 | 36.3(?) |
| 950 | 3.5 | 0.3 | 2.0 | 80 |
| 950 | 3.7 | 0.3 | 1.0 | 61.5(?) |
| 950 | 3.7 | 0.3 | 0.5 | 79 |
| 950 | 4.0 | 0.2 | 0.5 | 60.4(?) |

Example 3

In order to determine the optimal mole ratio of potassium nitrate to iron, various reactant formulations were prepared. Sedona Red iron oxide, potassium nitrate and potassium hydroxide at the concentrations shown in the table below were intimately mixed together via a ring mill. The resulting formulations were then heated in a muffle furnace at 950°C for a period of time which ranged between 0.5 and 1.0 hours. The reaction product was analyzed for the amount of iron(IV or greater) ferrate. The reactant formulations and percent of the iron converted to Fe⁺⁶ are found in the table below.

| °C | Moles KNO ₃ per Mole Fe ₂ O ₃ | Moles KOH per Mole Fe ₂ O ₃ | HOURS | % Converted to K ₂ FeO ₄ |
|-----|--|---|-------|--|
| 950 | 2.5 | 0 | 1 | 20 |
| 950 | 2.5 | 0 | 1 | 22 |
| 950 | 2.5 | 0 | 1 | 19 |
| 950 | 2.5 | 0 | 0.5 | 23 |
| 950 | 2.5 | 0 | 1 | 29 |
| 950 | 2.5 | 0.5 | 1 | 39(?) |
| 950 | 3.3 | 0.3 | 0.5 | 83 |
| 950 | 3.3 | 0.3 | 1 | 53 |

| | | | | |
|-----|-----|-----|-----|---------|
| 950 | 3.5 | 0.5 | 0.5 | 71 |
| 950 | 3.6 | 0.2 | 0.5 | 55.9(?) |
| 950 | 3.8 | 0.4 | 0.5 | 49.5 |
| 950 | 3.7 | 0.3 | 1 | 36.3(?) |
| 950 | 3.7 | 0.3 | 1 | 61.5(?) |
| 950 | 3.7 | 0.3 | 0.5 | 79 |
| 950 | 4 | 0.2 | 0.5 | 60.4(?) |
| 950 | 4.5 | 0.3 | 0.5 | 51 |
| 950 | 4.5 | 0.3 | 0.5 | 58 |
| 950 | 4.5 | 0.3 | 0.5 | 51 |
| 950 | 4.5 | 0.3 | 0.5 | 60(?) |

Example 4

In order to determine the effect of potassium hydroxide on the described reaction a number of reactant formulations were prepared. Sedona Red iron oxide, potassium nitrate at concentrations ranging from 3.5 to 3.8 moles KNO_3 to Fe_2O_3 , and potassium hydroxide concentrations from 0-0.5 moles KOH to Fe_2O_3 were mixed together via ring mill. The resulting formulations were heated in a muffle furnace to a temperature of 950°C for a period of time ranging from 0.5 to 1.0 hours. The reactant formulations and percent of the iron converted to Fe^{+6} are found in the table below.

| $^\circ\text{C}$ | Moles KNO_3 per Mole Fe_2O_3 | Moles KOH per Mole Fe_2O_3 | HOURS | % Converted to K_2FeO_4 |
|------------------|---|---|-------|---|
| 950 | 3.5 | 0.5 | 0.5 | 71 |
| 950 | 3.6 | 0.2 | 0.5 | 55.9 |
| 950 | 3.8 | 0.4 | 0.5 | 49.5 |
| 950 | 3.7 | 0.3 | 1 | 38.3(?) |
| 950 | 3.6 | 0 | 0.5 | 29 |

| | | | | |
|-----|-----|-----|--------|---------|
| 950 | 3.8 | 0 | 0.5 | 43 |
| 950 | 3.7 | 0.3 | 1 | 61.5(?) |
| 950 | 3.7 | 0.3 | 0.6(?) | 79 |

These examples demonstrate the importance of alkali metal nitrate and alkali metal hydroxide concentrations, as well as time and temperature to the reaction efficiency of the present invention. These examples indicate the benefits of including both potassium hydroxide in the reaction mixture at least at 0.2 mole KOH per mole Fe_2O_3 , and potassium nitrate in the reaction mixture at greater than 3.0 mole KNO_3 per mole Fe_2O_3 . The examples also demonstrated the importance of having a reaction temperature greater than 925°C and preferably at 950°C . It was also shown that reaction times from 0.5 and 2.0 are acceptable.

A wide range of reactant formulations could be created by one skilled in the art based on the teachings herein. A large number of permutations based on varying the reaction time and temperature can also be derived from the teachings found herein by one skilled in the art. These resulting embodiments are therefore considered to be within the scope of this invention.

While a preferred embodiment of the present invention has been described, it should be understood that various changes, adaptations and modifications may be made therein without departing from the spirit of the invention and the scope of the appended claims.

What is claimed is:

1. A method of making alkali metal ferrates, comprising:
suspending an oxidizable iron-containing particle reactant in a molten
phase comprising an alkali metal nitrate reactant and an oxy-alkali metal
5 reactant chosen from a group consisting of KOH, K_2O , K_2O_2 , K_2O_3 , KO_2 ,
NaOH, Na_2O , Na_2O_2 , Na_2O_3 , and NaO_2 ; and
reacting the reactants at a reaction temperature of from about 700°C to
about 1100°C.
2. The method of claim 1 wherein; said iron-containing particle reactant is
10 hematite ore including at least about 5% by weight of silicon dioxide.
3. The method of claim 1 wherein; said iron-containing particle reactant is
hematite ore including at least about 1% by weight of aluminum oxide.
4. The method of claim 1 wherein said iron-containing particle reactant is a
magnetite ore, a wustite ore, or iron-containing flue dust.
- 15 5. The method of claim 1 wherein said iron-containing particle reactant is an
iron oxide, potassium ferrite, or sodium ferrite.
6. The method of claim 1 including, before said heating step, the step of
forming an intimate mixture of iron oxide particles in reactive association
with said reactants.
- 20 7. The method of claim 6 wherein including the step of forming solid pellets
from said intimate mixture.
8. The method of claim 1 wherein said alkali metal nitrate reactant is
potassium nitrate or sodium nitrate.
9. The method of claim 1 wherein said alkali metal nitrate reactant is the
25 stoichiometric limiting reactant.
10. The method of claim 1 wherein said oxy-alkali metal reactant is di-
potassium oxide, potassium hydroxide, di-sodium oxide, or sodium
hydroxide.
11. The method of claim 1 wherein said reaction temperature is in the range
30 of from about 900°C to about 1000°C.

12. The method of claim 1, further comprising:
maintaining said reactants in said reaction temperature range for a period
of from about one minute to about three hours
13. The method of claim 1 wherein said reaction time is from about five
5 minutes to about thirty minutes.
14. The method of claim 1 wherein said iron-containing particle reactant and
said alkali metal nitrate reactant are present at a mole ratio ranging from
about 1:2 to about 1:5.
15. The method of claim 1 wherein said alkali metal nitrate reactant is in
10 molar excess of said oxy-alkali metal reactant in said formulation.
16. The method of claim 1, further comprising the step of:
cooling said reactants from said reaction temperature to a temperature
from about 500°C to about 800°C in a reaction atmosphere where the log
partial pressure of nitrogen is less than about 0.5 and the log partial
15 pressure of oxygen is between about -0.5 and about 1.5; and
retaining said reactants at such conditions for a time sufficient to reduce
remaining alkali metal nitrate in said reactants below about 5%.
17. The method of claim 16 wherein said reaction product is retained at such
conditions from 5 to 15 minutes.
- 20 18. The method of claim 16, further comprising flowing CO₂ into said reaction
atmosphere at a flow rate sufficient to maintain in said reaction
atmosphere a 1 to 2 mole ratio of CO₂ to KOH.
19. The method of claim 1, further comprising recovering nitrogen oxide
liberated during said reaction step, and converting said nitrogen oxide
25 into an alkali metal nitrate for reuse in said method.
20. The method of claim 1 further comprising the step of pulverizing resulting
alkali metal ferrate into a granular form.
21. A method of making potassium metal ferrates, comprising:
(a) suspending an oxidizable iron-containing particle reactant in a molten
30 phase comprising a potassium nitrate reactant and a potassium hydroxide
reactant, where the mole ratio between the iron oxide reactant and the

potassium nitrate reactant is about 1:2 to about 1:5; and said potassium nitrate reactant is in molar excess of said potassium hydroxide reactant; (b) reacting the product of (a) for a time from about five minutes to about thirty minutes at a reaction temperature of about, 800°C to 1000°C in a continuous feed kiln.

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22. The method of claim 21 further comprising:
cooling said reactants to a temperature from about 500°C to about 800°C in a reaction atmosphere where the log partial pressure of nitrogen less than about 0.5 and a log partial pressure of oxygen between about -0.5 and about 1.5;

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retaining said reactants at such conditions for a time sufficient to reduce remaining potassium nitrate in said reaction product below 5%;
pulverizing the resulting product into a granular form.

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23. A method of making alkali metal ferrates, comprising:
preparing a formulation comprising a source of oxidizable iron, an alkali metal nitrate reactant, and an oxy-alkali metal reactant chosen from a group consisting of KOH, K₂O, K₂O₂, K₂O₃, KO₂, NaOH, Na₂O, Na₂O₂, Na₂O₃, and NaO₂; and
reacting said formulation to a reaction temperature of from 700°C to 1100°C for a reaction time from about one minute to about three hours to produce a reaction product which contains greater than 60% alkali metal iron (IV or greater) ferrates by weight.

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24. A method of making potassium ferrates, comprising:
preparing a formulation in pellet form, wherein said formulation includes an iron oxide reactant, a potassium nitrate reactant, and a potassium hydroxide reactant, where the mole ratio between the iron oxide reactant and the potassium nitrate reactant is from about 1:2 to about 1:5; and said potassium nitrate reactant is in molar excess of said potassium hydroxide reactant;

reacting said formulation for a time from about ten minutes to about thirty minutes, said formulation to a reaction temperature of about 950°C in a continuous feed kiln;

cooling said reaction product to a temperature from about 500°C to about 800°C in a reaction atmosphere where the log partial pressure of nitrogen less than about 0.5 and a log partial pressure of oxygen between about - 0.5 and about 1.5;

retaining said reaction product at such conditions for a time sufficient to reduce remaining potassium nitrate in said reaction product below 5%;

pulverizing said reactants into a granular form; and

scrubbing nitrogen oxide gases released from said reactants during heating with an aqueous potassium hydroxide solution.

25. The method of making an alkali metal ferrate, comprising

preparing a formulation comprising an intimate mixture of a particulate iron oxide reactant, an alkali metal nitrate reactant, and an alkali metal hydroxide reactant, conveying said intimate mixture through a high

temperature reaction chamber in which said intimate mixture is maintained at a reaction temperature of at least about 700°C for a period ranging from one minute to 30 minutes to cause said reactants to react and convert at least 60% of particulate iron oxide reactant to iron (IV or greater) forms of iron oxide, and cooling the resulting product, and

wherein said high temperature reaction chamber includes a conveyor for conveying said intimate mixture into the reaction chamber and for conveying the resulting product out of the reaction chamber, the method including the step of continuously feeding said intimate mixture onto said conveyor and continuously removing the resulting product from said conveyor.

26. The reaction product resulting from the method of anyone of claims 1, 21, 23, and 24, the product including K_2FeO_4 and K_2FeO_3 ferrates in a combined molar concentration yielding a ratio of at least 1 to 1 moles of such ferrates per mole of Fe_2O_3 , and including not more than 1 to 10

moles of KNO_3 per mole of said combined ferrates, said product being in finely divided form.

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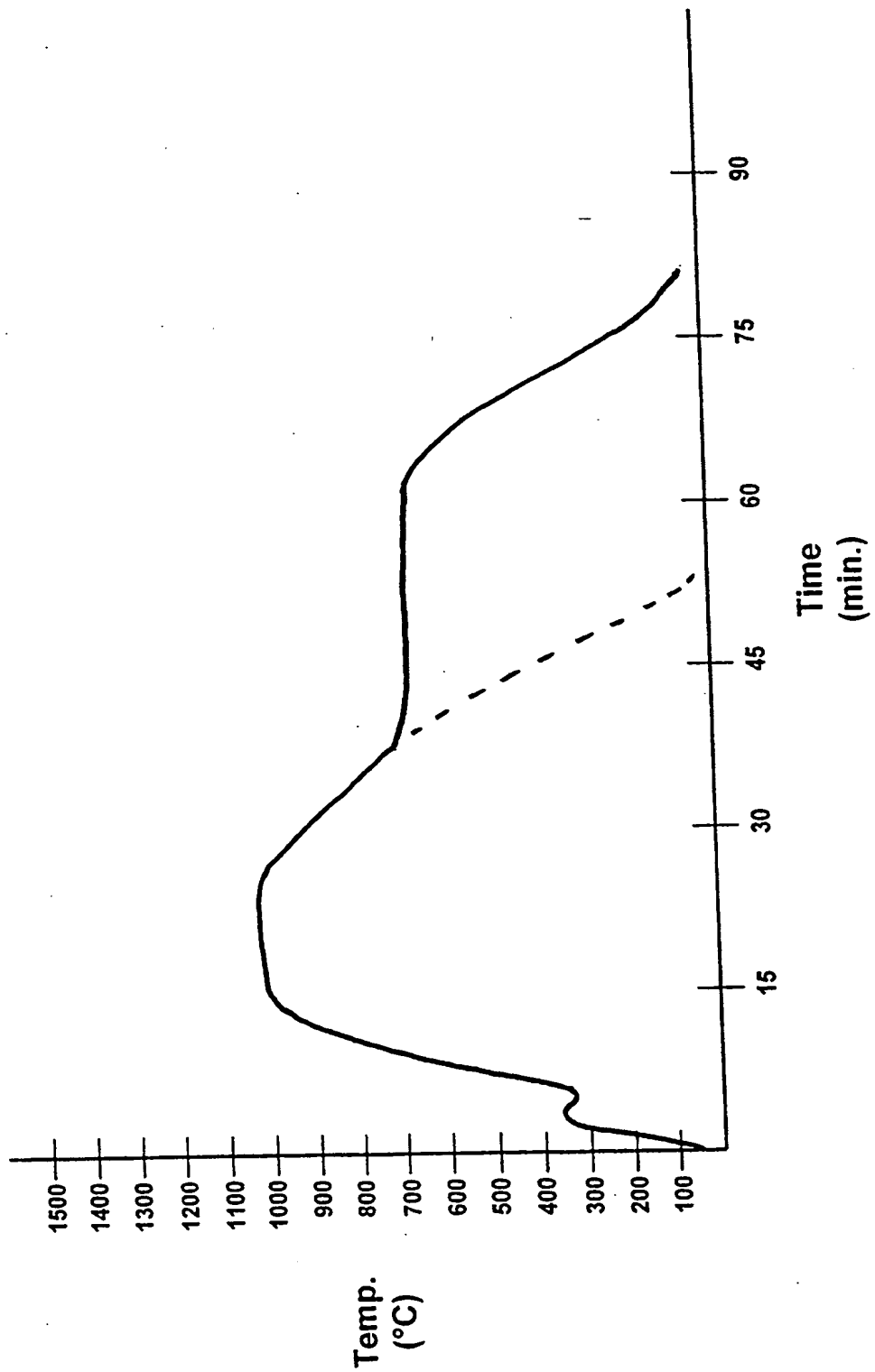
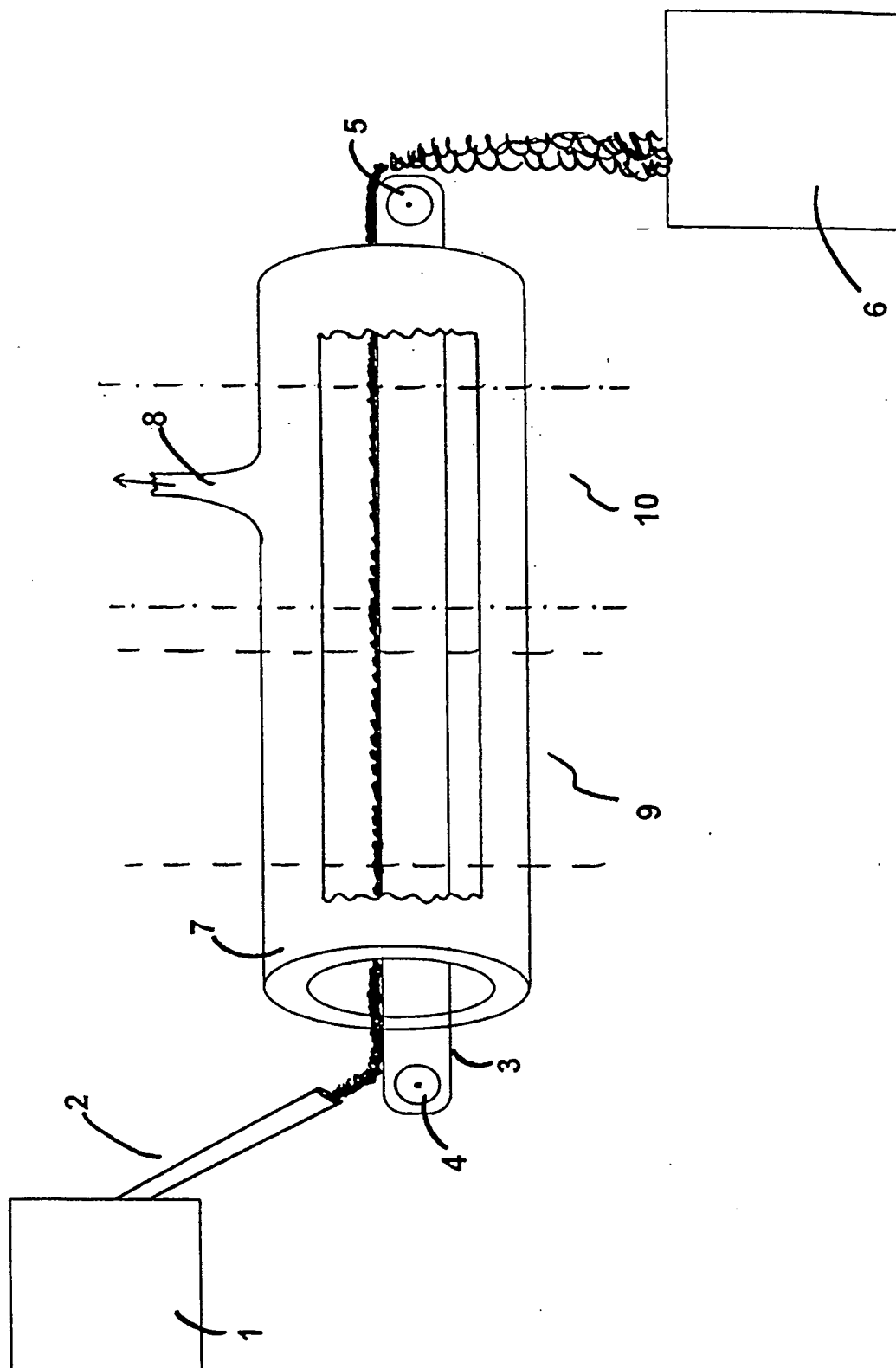
Figure 1

Figure 2



INTERNATIONAL SEARCH REPORT

In tional Application No
PCT/US 98/25683

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C01G49/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C01G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|--|-----------------------|
| Y | EP 0 155 837 A (THOMPSON JOHN ALFRED) 25 September 1985 cited in the application see claims 1-5 | 1,23 |
| Y | EP 0 059 622 A (THOMPSON JOHN ALFRED) 8 September 1982 cited in the application see claims 1-8 | 1,23 |



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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Date of the actual completion of the international search

27 April 1999

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INTERNATIONAL SEARCH REPORT

Int'l. Application No
PCT/US 98/25683

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|----------|---|-----------------------|
| A | <p>CHEMICAL ABSTRACTS, vol. 78, no. 16, 23 April 1973 Columbus, Ohio, US; abstract no. 99785, XP002101265 see abstract & NEREZOV: IZV.VYSSH.UCHEB.ZAVED.,TSVET.MET., vol. 15, no. 4, 1972, pages 17-21, ussr</p> <p style="text-align: center;">-----</p> | 1-4 |

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. .tional Application No

PCT/US 98/25683

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---------------------|------------------------------|--------------------------|
| EP 0155837 A | 25-09-1985 | US 4545974 A DE 3563528 A | 08-10-1985 04-08-1988 |
| EP 0059622 A | 08-09-1982 | US 4385045 A US 4551326 A | 24-05-1983 05-11-1985 |